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PRESSURE AND TEMPERATURE DEPENDENCE OF THE PROTON AND DEUTERON SPIN–LATTICE RELAXATION TIMES IN LIQUID H_2S AND D_2S

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The pressure and temperature dependence of the spin–lattice relaxation time T_1 for the protons in liquid H_2S and the deuterons in liquid D_2S have been measured between the melting-pressure-curve and 395 K at pressures up to 200 MPa. The different contributions to the experimental relaxation rate T_1^{-1} could be separated with the extended J-diffusion model. The results are compared with analogous measurements made previously in liquid water and liquid ammonia in order to get some insight into the influence of hydrogen bonding interactions upon molecular motions in these liquids. From the pressure dependence of the isotherms an activation volume of $\Delta V^{\ddagger} = 2 \pm 0.5$ [cm^3/mol] is derived for the rotational motion of the H_2S molecule, while the translational motion is characterized by a higher $\Delta V^{\ddagger} = 7 \pm 1$ [cm^3/mol].

1. Introduction

The hydrides of nitrogen, oxygen and fluorine form liquids with rather unique structures. The physical properties of these liquids are explained by the ability of these hydrides to participate in hydrogen bonding. The physical anomalies caused by the formation of extended hydrogen bond networks are most pronounced in the case of liquid water [1]. Liquid hydrogen sulfide, the higher homologue of water, does not reveal any hydrogen bonding ability. The molecular interactions in hydrogen sulfide are dominated mainly by dipole- and dispersion forces [2, 3], so that it may be regarded as a simple dipolar, non-associated liquid. Its molecular geometry is similar to the geometry of the water molecule [4, 5] as is its dipole moment (H_2O: 1.8×10^{-18} esu; H_2S: 1.1×10^{-18} esu; NH_3: 1.3×10^{-18} esu). Thus it may be hoped that comparison of the dynamic properties of these hydrides will yield some insight into the influence of hydrogen bonds upon the molecular motions in these liquids.

As is well known, NMR presents a suitable method for the study of molecular motions in liquids. Valuable information can be gained from the temperature and pressure dependence of spin–lattice relaxation times T_1. Previous NMR investigations of this substance have mainly been concerned with its properties in different solid phases [6–8]. Early T_1-measurements in liquid H_2S have been reported by Hennel et al. [9, 10] at saturation pressure p_s up to the critical point in H_2S. Recently Topol et al. [11, 12] presented T_1-measurements in H_2S along the coexistence line from the melting point to temperatures above the critical temperature T_c and found an anomalous temperature and frequency dependence of proton-T_1 near but above the critical temperature. The only T_1-measurements in D_2S have been reported by O'Reilly and Eraker [13] in the liquid phase between the melting point and the boiling point at atmospheric pressure and in the solid phases. No high pressure T_1-measurements have, to the best of our knowledge, been reported for H_2S or D_2S.

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2. Experimental

The deuteron and proton longitudinal relaxation times T_1 were obtained on a Varian XL-100-15 FT NMR spectrometer interfaced to a 16 K Varian 620L-100 computer with disk accessory by a t_1–90°–t_2–180°–t_1–90° pulse sequence. The observe frequency on this instrument is 100.1 MHz for protons and 15.4 MHz for deuterons. The modified variable temperature accessory of this spectrometer was used in the experiments. The temperatures were determined to ±0.5 K with a metal sheathed miniature chromel–alumel thermocouple. Deuterium sulfide was prepared by hydrolysis of degassed aluminium sulfide with 100% deuterium oxide [14], the isotopic purity as judged from the residual proton peak was >95%. Hydrogen sulfide was drawn from a lecture bottle. Both sulfides were distilled several times at low temperatures in a high vacuum apparatus. The gaseous sulfides were stored in the dark in a flask over phosphorus pentoxide. Prior to use, the sample was thoroughly degassed by at least five freeze–pump–thaw cycles to a final pressure of 7×10^{-3} Pa. Freezing was accomplished by immersing the probe into liquid nitrogen, the melting was done in acetone/carbon dioxide mixtures. The high pressure apparatus [15] and the elaborate filling procedure and apparatus [16] necessary for the oxygen-free filling of the high pressure capillaries have been described previously. The purity of the high pressure samples was controlled by comparison of the T_1-results obtained at saturation pressure with samples of H_2S and D_2S sealed in heavy walled 5 mm NMR tubes. No significant difference was found between the two sets of data. As controlled by repeated T_1-measurements under identical conditions, the sulfides in properly filled and assembled cells remain free of any contamination for several months. In the case of H_2S the proton T_1-data at p_s are also compared to published results [9, 10].

The measurements are judged reliable to ±10%, the reproducibility of the data was better than ±5%.

3. Theoretical

The dominant relaxation mechanisms for proton and deuteron relaxation in H_2S and D_2S are the direct dipole–dipole interaction, spin–rotation interaction and quadrupole interaction. The dipole–dipole interaction can be split into an intramolecular and an intermolecular contribution. In the case of proton T_1 the measured relaxation rate is given by

$$\frac{1}{T_1}=\frac{1}{T_1^{\text{intra}}}+\frac{1}{T_1^{\text{inter}}}+\frac{1}{T_1^{\text{SR}}}, \tag{1}$$

whereas the deuterium relaxation rate is given by

$$\frac{1}{T_1}=\frac{1}{T_1^{\text{Q}}}+\frac{1}{T_1^{\text{SR}}}. \tag{2}$$

In the fast motional limit [17] the dipolar and quadrupolar relaxation rates are given as [18–20]

$$\frac{1}{T_1^{\text{intra}}}=\frac{3}{2}\frac{\gamma^4\hbar^2}{r_{\text{HH}}^6}\tau_2, \tag{3}$$

$$\frac{1}{T_1^{\text{inter}}}=\tfrac{15}{4}\gamma^4\hbar^2 f_n\frac{\rho}{D}\int_0^\infty \mathrm{d}k\left[\int_0^\infty \mathrm{d}r g_{\text{HH}}(r)\frac{j_z(kr)}{r}\right]^2, \tag{4}$$

$$\frac{1}{T_1^{\text{Q}}}=\frac{3\pi^2}{2}\left(\frac{e^2qQ}{h}\right)^2\left(1+\frac{\eta_{\text{Q}}^2}{3}\right)\tau_2, \tag{5}$$

with

$$\tau_2=\int_0^\infty \mathrm{d}t\frac{\langle\mathscr{D}_{mn}^{(2)}|\mathscr{D}_{mn}^{(2)}(t)\rangle}{\langle[\mathscr{D}_{mn}^{(2)}]^2\rangle},$$

and $\mathscr{D}$ a Wigner rotation matrix describing the orientation of a molecule fixed coordinate system relative to the laboratory system, r_{HH} is the proton–proton distance in the molecule, ρ is the density of the system, D is the self-diffusion coefficient, f_n is the fractional abundance of the magnetic nuclear species, $j_z(kr)$ is a Bessel-function, $g_{\text{HH}}(r)$ the static pair distribution function, e^2qQ/h is the quadrupole coupling constant and η_{Q} the asymmetry parameter of the traceless field gradient tensor.

Theoretical expressions for the spin–rotation relaxation rate applicable to an asymmetric top are available in the literature within the rotation diffusion model only [21], which, as will be discussed later, seems not to be applicable in the case of H_2S and D_2S. For a spherical top the relaxation rate is given as [22–24]

$$\frac{1}{T_1^{SR}} = \frac{8\pi^2 I k_B T}{\hbar^2}(C_0^2\tau_J + 2\Delta C^2\tau_{SR}), \tag{6}$$

with τ_J the correlation time for the angular momentum autocorrelation function and τ_{SR} the correlation time of the angular velocity-orientational product correlation function which characterizes anisotropic spin-rotational interactions,

$$C_0 = \tfrac{1}{3}(C_{xx} + C_{yy} + C_{zz})$$

and

$$\Delta C = \tfrac{1}{3}[C_{zz} - \tfrac{1}{2}(C_{xx} + C_{yy})]$$

are combinations of the elements of the spin rotation tensor and I is the mean moment of inertia calculated according to

$$I^{-1} = \tfrac{1}{3}(I_x^{-1} + I_y^{-1} + I_z^{-1}).$$

Table 1 collects the relevant molecular constants needed in the equations given above.

Table 1

	H_2S	D_2S	Ref.
$r_{H\text{-}H}$ [Å]	1.883±0.007		[5]
e^2qQ/h [kHz]		149	[4]
η_Q		0.197	
C_0^2 [s^{-2}]	2.94×10^8	1.86×10^6	[4, 5, 38]
ΔC^2 [s^{-2}]	1.52×10^6	8.71×10^3	[4, 5, 38]
$\langle I\rangle$ [kg m^2]	3.48×10^{-47}	6.75×10^{-47}	[5]

The elements of the spin-rotation tensor $\mathbf{c}$ for H_2S have been calculated with the relation $C_{gg'} = g_I\Lambda_{gg'}B_g$ and $\Lambda_{gg'}$ as given in ref. [4] and the rotational constants B_g given in ref. [5] and g_I the nuclear g-factor [38]. The elements of the moment of inertia tensor $\mathbf{I}$ have been calculated from the rotational constants B_g ($v=0$) given in ref. [5] and the relation $I_g = h/8\pi^2B_g$, $\langle I\rangle$ has been calculated with the relation, $1/\langle I\rangle = \frac{1}{3}\sum_{g=a,b,c}(1/I_g)$.

4. Results and discussion

The spin–lattice relaxation times T_1 of the protons in H_2S and the deuterons in D_2S have been measured. The temperature has been varied from the melting pressure curve to 395 K and pressures up to 200 MPa have been applied. The relaxation times measured are collected in tables 2 and 3, the temperature dependences of the relaxation times in H_2S and D_2S are shown for saturation pressure and $p =$ 200 MPa in fig. 1.

4.1. Separation of different relaxation rates

Regarding for simplicity D_2S as a spherical molecule and inserting the pertinent molecular constants (table 1) into the theoretical expressions (5) and (6) the experimental relaxation rate is given by

$$1/T_1 = 3.33\times10^{11}[s^{-2}]\tau_2[s] + 1.23\times10^7[K^{-1}s^{-2}]T[K]\tau_J[s] + 1.15\times10^5[K^{-1}s^{-2}]T[K]\tau_{SR}[s]. \tag{7}$$

Because $\tau_{SR} \leq \tau_J$ [23, 24] and $\Delta C^2 \ll C_0^2$ this expression can be approximated by

$$1/T_1 \approx 3.33\times10^{11}\tau_2 + 1.23\times10^7 T\tau_J. \tag{8}$$

Theoretical models dealing with rotational motions of molecules in fluids [25–28] do show that τ_2 and τ_J are not independent, but that τ_2 has to be regarded as a function of τ_J. This leaves only one free parameter in eq. (8).

Consequently the temperature and pressure dependence of T_1 should provide a useful test for different diffusion models, although it is hardly possible to determine experimentally both correlation times independently. An additional constraint on these models is the measurement of different isotopes of the same molecular species since any model capable of describing the temperature and pressure dependence of the deuteron-T_1 in D_2S must also be able to account consistently for the temperature and pressure dependence of the proton-T_1 in H_2S. Assuming that the reduced correlation times $\tau^* = \tau(k_BT)^{1/2}/I$ are at constant p, T

Table 2
Experimental spin-lattice relaxation times (T_1 (s)) in H_2S

T (K)	P (bar)				
	100	500	1000	1500	2000
198	22.5				
211	25.5	23	20		
219			21.5		
222	27.5				
225				19.5	
227		25.5			
229					18.5
232			24	20	
236	28				
237				21	
238		27.5			19.5
243			25		
247	28.5	27			
252				23	
255			26.5		21.5
260	28				
266			27		
267				24.5	
269					23.5
274	27	27			
277				25.5	
280			26.5		
286					24
292				26	
302	25	26			
303					24.5
305			26		
310				26	
321					24
340			24.5	24.5	24
341	20	23			
393	5	16.5	18.5	19.5	20.5

saturation pressure

T (K)	198	208	222	236	247	260	279	308
T_1 (s)	22	25.5	28	28	28.5	28	26.5	24.5

393 K:

p (bar)	100	150	200	250
T_1 (s)	5	12	14	15

identical for both substances yields after insertion of the appropriate molecular constants in eqs. (3), (5) and (6) the following relations:

$$\frac{1}{T_1^{Q}}(D_2S) = 24.11\,\frac{1}{T_1^{intra}}(H_2S), \tag{9}$$

Table 3
Experimental deuterium spin-lattice relaxation times (T_1 (s)) in D_2S

T (K)	P (bar)				
	100	500	1000	1500	2000
204	20.5				
220		22.5	20.5		
226	24.5				
230				22	
236					22
237		25			
238			24		
250	28.5		25.5		
251		26.5		25	
258					25
271			28		
272	31				
273		29.5			
275				29	
278					27
293	34	32			
294			32	31	
295					30
309	36	35			
324					32
326	38	37	36	34	
359				37	37
360	36	39	38		
394		39	40	39	40
396	32				

saturation pressure

T (K)	193	208	223	240	257	273	291	307
T_1 (s)	18	22	24	26.5	29	31	34	36

394 K: 250 bar: $T_1 = 34$ s

$$\frac{1}{T_1^{SR}}(D_2S) = 1.73\times10^{-2}\,\frac{1}{T_1^{SR}}(H_2S). \tag{10}$$

After separation of the contributions from the intramolecular quadrupole and spin-rotation relaxation mechanism to the experimental relaxation rate in D_2S the intramolecular dipole–dipole relaxation rate as well as the spin-rotation contribution are obtained for H_2S from eqs. (9) and (10). The relaxation rates for all three mechanisms contributing to the measured relaxation rate in the case of H_2S can therefore be calculated with eqs. (1), (9) and (10).

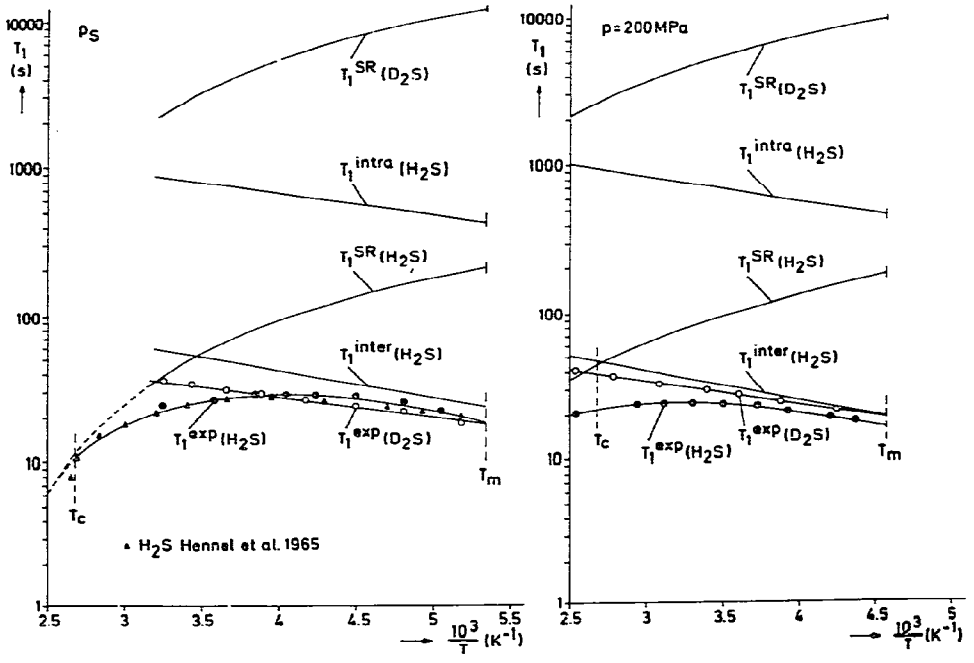

Fig. 1. Temperature dependence of the experimental relaxation times T_1 in H_2S (—●—) and D_2S (—○—) together with the estimated contributions from the different relaxation mechanisms for saturation pressure p_s and $p = 200$ MPa. T_1-data for H_2S at p_s from refs. [9, 10] are included for comparison.

In order to separate with eq. (8) the relaxation rates in the case of D_2S a model for the molecular rotational motion must be chosen to provide the functional relationship between τ_2 and τ_J. The extended J-diffusion (EDJ) model [22, 29], the Fokker–Planck–Langevin (FPL) model [23] and the rotational diffusion (RD) model [19, 27] have been tested. Among these models the EDJ-model only permits the description of all different isobars with a physically acceptable temperature dependence of $(T_1^Q)^{-1}$ and $(T_1^{SR})^{-1}$. The necessary parameters τ_J^* to fit the D_2S data with eq. (8) are compiled in table 4. The related quantities τ_2^* can either be calculated with an equation given by McClung [22] or simply taken from a graph $\tau_2^*(\tau_J^*)$ drawn with the values tabulated by Powles and Rickayzen [26]. It should be noted that even at $T \approx T_m$ the parameters τ_2^*, τ_J^* necessary to fit the data are beyond the range where all models merge into the rotational diffusion limit, that is they do not obey the Hubbard relation [30].

In the case of both the FPL- and the RD-model large changes in the parameter τ_J^* in the region of the maximum of the T_1-isobars are necessary to fit the measured temperature dependence of T_1 in D_2S with eq. (8). Moreover the resulting $T_1^{SR}(H_2S)$ estimated with eq. (10) became shorter than the experimental relaxation times for H_2S which is unacceptable.

Although the temperature dependence of T_1 in D_2S can be described quantitatively with the EDJ-model, the resulting relaxation times T_1^Q are close to the experimentally determined T_1 even on the high temperature side of the maximum of the isobars. This behaviour may be due to a deficiency of the separation procedure but every relaxation rate $1/T_1^{SR}$ large enough to remove the minimum in the $1/T_1^Q$-isobars of

Table 4

$p = p_s$		$p = 10$ MPa		$p = 50$ MPa		$p = 100$ MPa		$p = 150$ MPa		$p = 200$ MPa	
T (K)	τ_J^*	T (K)	τ_J^*	T (K)	τ_J^*	T (K)	τ_J^*	T (K)	τ_J^*	T (K)	τ_J^*
193	0.25	204	0.27	220	0.29	220	0.26	230	0.275		
208	0.29	226	0.35	237	0.34	238	0.32			236	0.265
223	0.34	250	0.44	251	0.37	250	0.34	251	0.33	258	0.32
240	0.40	272	0.54	273	0.44	271	0.39	275	0.40	278	0.37
257	0.47	293	0.62	293	0.53	294	0.50	294	0.46	295	0.42
273	0.55	309	0.80	309	0.64						
291	0.65	326	0.95	326	0.75	326	0.63	326	0.56	324	0.48
307	0.80	360	1.50	360	1.00	360	0.84	359	0.69	359	0.59
		396	2.25	394	1.35	394	1.05	394	0.93	394	0.77

D_2S proved, after transformation with eq. (10), to be larger than $1/T_1^{exp}$ for H_2S, which of course is physically impossible. It is to be expected that the relaxation time T_1 in D_2S possesses a weak anomaly in the vicinity of the critical temperature similar to that found in the case of H_2S by Topol et al. [11, 12]. These authors measured a sharp rise in the proton-relaxation rate $1/T_1$ in H_2S near but above the critical temperature. However, our experimental equipment does not permit sufficiently precise measurements around T_c to resolve this question. Thus in the subsequent discussion we will focus our attention on the behaviour of the relaxation times T_1 at temperatures $T < T_c$.

The isobaric temperature dependence of the relaxation times corresponding to the different relaxation mechanisms in D_2S and H_2S are shown in fig. 1 for $p = p_s$ and $p = 200$ MPa only. They cannot be expected to be very precise since in view of the difference in the relative strength of the relaxation mechanisms operative in D_2S ($3.33 \times 10^{11} \gg 1.23 \times 10^7\ T$) the T_1^{SR} estimated may contain a relatively large error. The separation procedure presented here obviously cannot provide a critical test of the different diffusional models considered. Not withstanding these difficulties in the case of D_2S the experimental relaxation rates are almost entirely due to quadrupolar relaxation so that T_1^Q is not included in fig. 1. The spin-rotational contribution as obtained with the EDJ-model (in fact every model should lead to analogous results in this respect) is completely negligible due to the smallness of the components of the spin-rotation coupling tensor $\mathbf{c}$. As can be seen from fig. 1, this does not hold for the protons of hydrogen sulfide. The spin-rotational relaxation in H_2S contributes significantly to the total relaxation rate of the protons and becomes the dominating relaxation mechanism at temperatures near the critical temperature T_c. At low temperatures the intermolecular dipolar interaction is the dominating relaxation mechanism, whereas the intramolecular dipolar interaction is the least effective relaxation mechanism at all temperatures and pressures. This is a consequence of the fast rotational motions of the molecules in liquid H_2S and D_2S which result in very short effective correlation times τ_2. The relative magnitude of inter- and intramolecular dipolar relaxation rates in hydrogen sulfide contrasts markedly with the behaviour of these quantities in liquid ammonia and liquid water as can be illustrated by the ratio of these relaxation rates in these systems at their respective melting points for $p = p_s$

$$R_1^{inter}/R_1^{intra} \approx 0.5 \quad \text{for } H_2O,$$
$$\approx 18 \quad \text{for } H_2S,$$
$$\approx 1.8 \quad \text{for } NH_3.$$

However a concise discussion of the intermolecular relaxation rate in these systems in terms of eq. (4) must await a thorough experimental determination of the constituent quantities in this expression especially in the case of hydrogen sulfide.

A discussion of the results presented here in terms of the density dependence of the parameters involved in the various models [31] is not possible at present due to the lack of experimental densities for H_2S and D_2S at pressures substantially higher than p_s. For example fig. 2 shows that the density dependence of the parameter $(\tau_J^*)^{-1}$ at saturation pressure [37] follows closely the density dependence of $(\tau_\omega^*)^{-1}$ calculated within the rough hard sphere model [25] with a hard sphere diameter σ between 3.95–4 Å. These values are close to the molecular diameters calculated from

liquid density at $T = 192$ K: $2a = 4.34$ Å,

viscosity of the gas: $2a = 4.32$ Å,

van der Waals constant b: $2a = 3.24$ Å,

crystal structure (solid I): $2a = 4.1$ Å.

It is also close to the parameter $\sigma = 3.405$ Å [32] in the Lennard-Jones potential of argon with which hydrogen sulfide is isoelectronic. Thus it may well be that the rough hard sphere fluid represents a useful approximation to real liquid hydrogen sulfide.

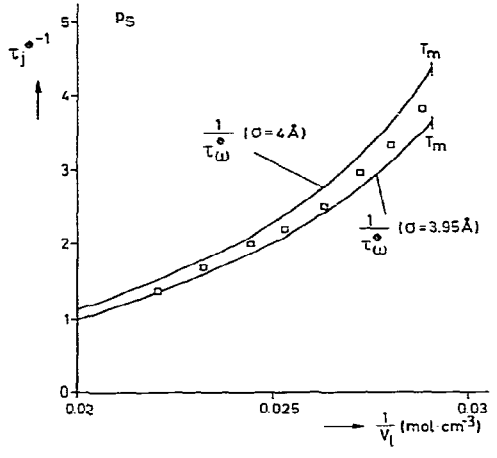

Fig. 2. Density dependence of $(\tau_J^*)^{-1}$ for saturation pressure p_s and $(\tau_\omega^*)^{-1}$ versus density for the rough hard sphere fluid as calculated with eqs. (3.2)–(3.4) and (3.17) given in ref. [25] for $\sigma = 3.95$ Å and $\sigma = 4$ Å. The molar volumes of D_2S at saturation pressure have been taken from ref. [37].

4.2. Pressure and temperature dependence of the relaxation times

As can be seen from fig. 1 the isobaric temperature dependence of T_1^Q, T_1^{intra} and T_1^{inter} show simple Arrhenius-behaviour at low temperatures. The slope of the isobars leads to an apparent "activation enthalpy" defined through the relation

$$\Delta H^{\ddagger} = R \left. \frac{\partial \ln (1/T_1)}{\partial (1/T)} \right|_p ,$$

which amounts to

T_1^Q, T_1^{intra}: $\Delta H^{\ddagger} = 3 \pm 0.2$ [kJ/mol],

T_1^{inter}: $\Delta H^{\ddagger} = 4 \pm 0.2$ [kJ/mol].

This has to be compared with the mean thermal energy at $T = 395$ K: $RT \approx 3.3$ [kJ/mol] and at $T = 200$ K: $RT \approx 1.66$ [kJ/mol]. The comparison shows that the description of the molecular motions in liquid hydrogen sulfide as activated processes is not applicable. O'Reilly et al. [13] obtained an activation energy of $E_A = 3.7$ [kJ/mol] for ^2H–T_1 in solid D_2S. Thus rotational motions of the molecules are only slightly more hindered in the solid I phase than in the liquid phase. From neutron scattering data in liquid H_2S Rzany and Sciesimski [3] estimated an interaction energy of $E = 1.9$ [kJ/mol] due to permanent dipole interactions. Thus these interactions contribute significantly to the hindrance of rotational motions of H_2S molecules in the liquid. As the permanent dipole moments of H_2O and NH_3 are not much different from that of H_2S, comparison of the barriers to rotational motions in these systems indicates the dominating influence of hydrogen bonding interactions upon these molecular motions. Fig. 3 compares the temperature dependence of ^2H T_1 in D_2S, ND_3 [16] and D_2O [33] at saturation pressure and at $p = 200$ MPa. The relaxation times T_1 are shown in an Arrhenius-plot over the reduced inverse temperature $1/T_r = T_c/T$ (T_c = critical temperature). Obviously the influence of hydrogen bonding interactions upon molecular motions in the associated dipolar fluids ND_3 and D_2O lead to significantly higher apparent activation enthalpies. Whereas in liquid D_2S and ND_3

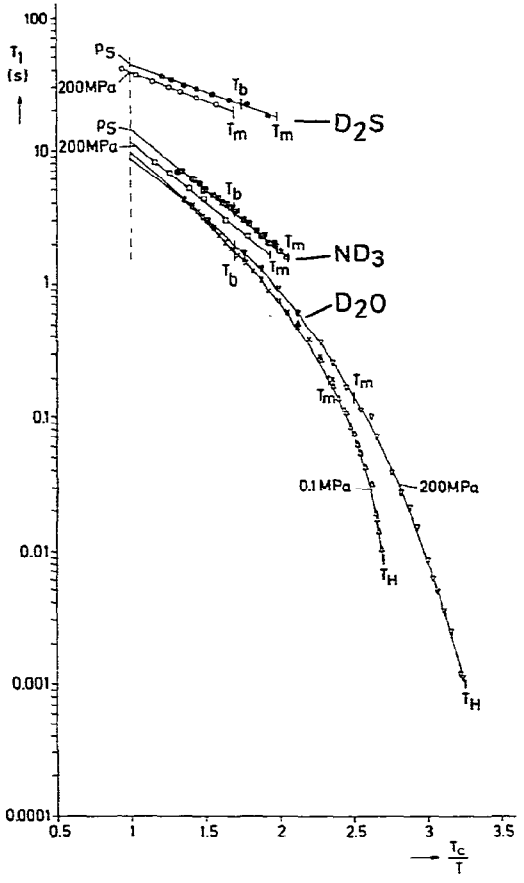

Fig. 3. $T_1(^2H)$ for D_2O, D_2S and ND_3 versus reduced inverse temperature $1/T_r = T_c/T$. T_m – melting point temperature, T_b – boiling point temperature under atmospheric pressure, T_H – homogeneous nucleation temperature [1], △, ▽ data from ref. [33], ▲, ▼ data from ref. [39], × data calculated with a two exponential fit equation given in ref. [40], □, ▣ data from ref. [16].

[16] this parameter is virtually constant over the whole range of temperatures and pressures measured, it becomes temperature- and pressure-dependent in the hydrogen bonded network-liquid water. Furthermore comparison of the reduced correlation times τ_2^* should reflect also the influence of hydrogen bonds upon molecular mobility:

	D_2O	D_2S	ND_3	
τ_2^*	86	1.03	6.5	$T = T_m, p = p_s$
	12	0.89	3.8	$T_r = 0.56, p = p_s$

Obviously the effective time constant for orientational fluctuations in hydrogen sulfide is very short, which shows again that the reorientational motions are only slightly hindered, whereas hydrogen bonds block these motions appreciably in the associated liquids especially in the network-liquid water. Regarding the pressure dependence of the relaxation times one can define an "activation volume" $\Delta V^{\ddagger}$ through the relation:

$$\Delta V^{\ddagger} = RT \frac{\partial \ln (1/T_1)}{\partial p}\bigg|_T .$$

At temperatures $T \leq 325$ [K] $\Delta V^{\ddagger}$ is within experimental error independent of pressure for both $1/T_1^Q$, $1/T_1^{intra}$ (fig. 4) and $1/T_1^{inter}$ (fig. 5) and at $T = 300$ K ($T_r = 0.8$) amounts to $\Delta V^{\ddagger}_{intra} = 2 \pm 0.5$ [cm^3/mol] and $\Delta V^{\ddagger}_{inter} = 7 \pm 1$ [cm^3/mol]. Comparison with $\Delta V^{\ddagger}$ obtained in liquid ammonia [16] shows that in both liquids $\Delta V^{\ddagger}_{intra}$ is nearly equal at the same reduced temperatures, but that $\Delta V^{\ddagger}_{inter}$ is somewhat higher in hydrogen sulfide than in

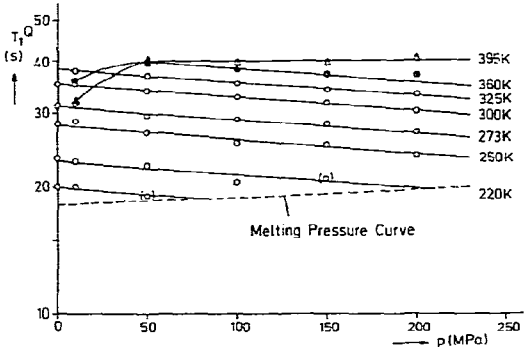

Fig. 4. Isotherms of the relaxation times T_1^Q of the intramolecular quadrupole relaxation mechanism in D_2S. The corresponding relaxation time T_1^{intra} of the intramolecular dipole–dipole relaxation mechanism possesses an identical pressure dependence according to eq. (9).

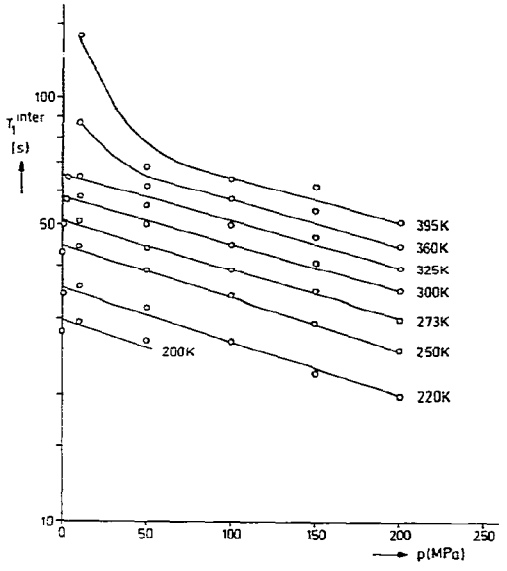

Fig. 5. Isotherms of the relaxation times T_1^{inter} of the intermolecular dipole–dipole relaxation mechanism in H_2S.

liquid ammonia. However, in both liquids the pressure dependence of the translational motions, as reflected in the parameter $\Delta V^{\ddagger}_{inter}$, is larger than the corresponding pressure dependence for the reorientational motions. $\Delta V^{\ddagger}$ may be regarded as a qualitative measure of the space required by a molecule to reorient or translate to a new position in the cage of its next neighbours. Thus $\Delta V^{\ddagger}_{inter} > \Delta V^{\ddagger}_{intra}$ indicates that translational diffusion is slowed down faster with increasing density than is rotational diffusion.

5. Conclusions

The spin–lattice relaxation times in liquid H_2S and D_2S have been measured since its molecular geometry and molecular parameters (table 1) are similar to those of the water molecule but its intermolecular interactions are not dominated by hydrogen bonding interactions. Thus a study of its dynamic behaviour as a function of temperature and pressure should help to understand the contribution of hydrogen bonds to the hindrance of rotational and translational motions of the molecules in the liquid phase. The effective correlation times of orientational fluctuations in H_2S and D_2S are very short ($\tau_2 \approx 10^{-14}$ s). The reduced effective time constants τ_2^*, which measure the correlation times of the fluctuations relative to those of a hypothetical free rotor, obey at all temperatures and pressures measured the relation $\tau_2^* \leqslant 1$. This shows that rotational motions in this liquid must proceed rather freely. The corresponding correlation times in liquid ammonia [16] are an order of magnitude longer and in liquid water they increase for identical reduced conditions by more than two orders of magnitude [33, 34]. Furthermore, fig. 3 shows a much stronger isobaric temperature dependence of the correlation times in the associated liquids ND_3 and D_2O than in the non-associated liquid D_2S. A comparison of the "activation enthalpies" obtained for rotational and translational motions in H_2S, H_2O [34] and NH_3 [16] reveals, that the concept of an activated process is certainly not applicable to transport phenomena in liquid H_2S, since the barrier to rotations is comparable to the mean thermal energy.

Unfortunately due to the lack of measured densities at pressures $p > p_s$ a more thorough discussion of the density dependence of the correlation times τ_2 and τ_J [25, 31, 35, 36] was not possible. The finding, that the data could be described with the EDJ-model does not present a critical test of this model because the data treatment had to rely on the estimation of the spin-rotational relaxation rate in D_2S where it makes only a minor contribution to the total relaxation rate. However, the condition that any model must describe the pressure and temperature dependence of the relaxation times in D_2S as well as in H_2S consistently led to the exclusion of the FPL- and the RD-model. This may however be due to the unavailability of a theoretical treatment of rotational motions for an asymmetric top which hydrogen sulfide in fact is. Some of the difficulties of the present separation procedure would be removed if self-

diffusion coefficients and static proton–proton pair-correlation functions or shear viscosities would be available over the range of temperatures and pressures measured. This would allow one to estimate, at least approximately, the intermolecular dipolar relaxation rate and thus provide an alternative separation of the different relaxation rates. Furthermore a comparison of the influence of the structure of liquid hydrogen sulfide, liquid ammonia and liquid water in terms of eq. (4) on the dynamical behaviour of the molecules in these liquids would become possible.

The high temperature maximum of ^{2}H T_1 in D_2S, its reduction with increasing pressure, and complete disappearence at pressures $p \geq$ 200 MPa is interesting since it cannot be explained by a balance of T_1^{SR} and T_1^{Q} in D_2S. In fact any reasonable estimate of T_1^{SR} fails to remove the maximum in T_1^{Q}. This indicates an anomalous temperature dependence of T_1^{Q} in D_2S at high temperatures and low pressures. Whether this anomaly is analogous to the one found above T_c in H_2S [11] deserves further careful measurements at high temperatures.

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References

[1] C.A. Angell in: Water – a comprehensive treatise, Vol. 7, ed. F. Franks (Plenum Press, New York 1981).
[2] J.C. Hindman, A. Svirmickas and W.B. Dixon, J. Chem. Phys. 47 (1967) 4658.
[3] H. Rzany and J. Sciesinski, Physica 29 (1963) 488.
[4] F.C. DeLucia and J.W. Cederberg, J. Mol. Spectry. 40 (1971) 52.
[5] R.L. Cook, F.C. DeLucia and P. Helminger, J. Mol. Struct. 28 (1975) 237.
[6] Z.M. El Saffar and P. Schultz, J. Chem. Phys. 56 (1971) 2524.
[7] J.H. Loehlin, P.G. Mennitt and J.S. Waugh, J. Chem. Phys. 44 (1966) 3912.
[8] D.C. Look, I.J. Lowe and J.A. Northby, J. Chem. Phys. 44 (1966) 3441.
[9] J.W. Hennel, A. Jasinski, S. Sagnowski and T. Waluga, Acta Phys. Polon. 28 (1965) 673.
[10] J.W. Hennel and T. Waluga, Bulletin Ampère 10 (1961) 366.
[11] R. Topol, K. Krynicki and J.G. Powles, Mol. Phys. 37 (1979) 1655.
[12] R. Topol, Mol. Phys. 40 (1980) 161.
[13] D.E. O'Reilly and J.H. Eraker, J. Chem. Phys. 52 (1970) 2407.
[14] M. Bandler, in: Handbuch der Präparativen Anorganischen Chemie, ed. G. Brauer (Stuttgart, 1975).
[15] G. Völkel, E. Lang and H.-D. Lüdemann, Ber. Bunsenges. Physik. Chem. 83 (1979) 722.
[16] H. Hauer, E. Lang and H.-D. Lüdemann, Ber. Bunsenges. Physik. Chem. 83 (1979) 1262.
[17] A. Abragam, The principles of nuclear magnetism (Oxford Univ. Press, London, 1961).
[18] M.D. Zeidler, Ber. Bunsenges. Physik. Chem. 75 (1971) 229.
[19] H.W. Spiess, in: NMR-basic principles and progress, Vol. 15, eds. P. Diehl, E. Fluck, R. Kosfeld (Springer, Berlin, 1978).
[20] D. Pumpernick and A. Azman, Chem. Phys. Letters 34 (1975) 438.
[21] C.H. Wang, Mol. Phys. 28 (1974) 801.
[22] R.E.D. McClung, Advan. Mol. Relaxation Inter. Processes 10 (1977) 83.
[23] R.E.D. McClung, J. Chem. Phys. 73 (1980) 2435.
[24] G. Lévi, J.P. Marsault, F. Marsault-Hérail and R.E.D. McClung, J. Chem. Phys. 73 (1980) 2443.
[25] J. O'Dell and B.J. Berne, J. Chem. Phys. 63 (1975) 2376.
[26] J.G. Powles and G. Rickayzen, Mol. Phys. 33 (1977) 1207.
[27] J. McConnell, Rotational brownian motion and dielectric theory (Academic Press, London, 1980).
[28] D.E. O'Reilly, J. Chem. Phys. 63 (1975) 3177.
[29] D. Chandler, J. Chem. Phys. 60 (1974) 3508.
[30] P.S. Hubbard, Phys. Rev. 131 (1963) 1155.
[31] J. Jonas, Ann. Rev. Phys. Chem. 26 (1975) 167.
[32] I.R. McDonald and K. Singer, J. Chem. Phys. 50 (1969) 2308.
[33] E. Lang and H.-D. Lüdemann, Ber. Bunsenges. Physik. Chem. 84 (1980) 462.
[34] E. Lang and H.-D. Lüdemann, J. Chem. Phys. 67 (1977) 718.
[35] W.J. Lamb and J. Jonas, J. Chem. Phys. 74 (1981) 913.
[36] J.J. van Loef, Physica 103B (1981) 133.
[37] E.C.W. Clarke and D.N. Glew, Can. J. Chem. 48 (1970) 764.

[38] A. Carrington and A.D. McLachlan, Introduction to magnetic resonance (Harper and Row, New York, 1969).

[39] J. Jonas, T. DeFries and D.J. Wilbur, J. Chem. Phys. 65 (1976) 582.

[40] J.C. Hindman, J. Chem. Phys. 60 (1974) 4488.